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TRACE CHEMICAL THREAT DETECTION BY ULTRAVIOLET MULTIPHOTON INDUCED FRAGMENT FLUORESCENCE

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

ArF excimer laser radiation has been used to dissociate dimethylmethylphosphonate (DMMP) and diethylmethylphosphonothioate (DEMPS) into electronically excited fragments. Spectrally resolved UV and visible emission identifies the excited fragments from DMMP as C, C_2 and CH and those from DEMPS as C_2, CH, PO and possibly PS and CS. In the few cases tested, the emission intensity is linear with respect to parent molecule concentration and persists in the presence of 100 torr of air. The excited fragment emissions could be the basis of a sensitive detection technique for these or similar molecules.

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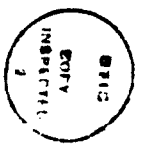
1. THE PROBLEM OF CHEMICAL THREAT DETECTION

The potential use of chemical agents, including biological toxins, in warfare or in terrorist activities is a potent threat to the security of our nation's military forces as well as those of friendly or neutral nations. These weapons also threaten civilian populations unfortunate enough to reside near the areas where such weapons are manufactured, transported, stored, or most seriously, actually employed.

Recent history adds to the sense of urgency, since, despite efforts to outlaw the use of chemical and biological weapons by international convention, the last 15 years have yielded serious evidence of the use of phosgene or related blister agents in South Yemen, nerve gases and incapacitating agents in Afghanistan, and mycotoxins in Southeast Asia.

The problem is obviously compounded by the variety of potential agents now available. These include the organophosphorus nerve gases, chlorine containing vesicant (blister) agents such as phosgene, mustard gas, or Lewisite, organic carbonyl incapacitating agents, lachrymators (tear-gases), emetic agents, and a wide variety of biological toxins, including the recently newsworthy mycotoxins. There is the additional serious concern that the enemy may have and use agents previously unknown to us.

This variety of chemical threats is further compounded by the range of physical forms possible for many agents. Some agents may be environmentally dispersed as gases, others as liquid droplets, some as pure aerosols or adsorbed onto aerosol substrates. They may still be significant threats when present as adsorbed liquid or solid contaminants on various surfaces.



Major efforts to develop techniques to detect and quantify chemical threat agents have been underway for some time at the Army's Chemical Research and Development Center (CRDC). These efforts have encompassed both point source and remote detection techniques. Operational point source detection schemes based on chemical or mass spectroscopic methods are available for a number of threats, however they are bulky, require frequent recharging and lack versatility. A sigificant level of in-house and contractor effort has also been expended on experimental remote detection techniques which have recently been reviewed by Flanigan and Phelps.[1] The remote techniques receiving the greatest current attention are passive Fourier Transform Infrared (FTIR) detection with linear discriminant processing and active differential laser backscattering techniques (DIAL/DISC).

Other advanced techniques for point source detection and analysis involving laser-induced multiphoton ionization with ion detection or laser-induced plasma breakdown followed by atomic fluorescence detection are currently being explored at the basic research level.[2] In general, the lack of reliable detection and analysis techniques sensitive to a wide variety of specific and generic chemical threat agents motivates the desire to develop new and powerful methods for evaluation.

In this report, we present the results of a modest set of experiments demonstrating the potential of a candidate detection and analysis technique which may have the capability of both general and extremely sensitive detection of trace chemical threats. When fully developed, the experiments reported here may allow the construction of a new point source detection and alarm system for a wide variety of current and potential threat agents.

The detection scheme to be evaluated is ultraviolet multiphoton induced fragment fluorescence or UV-MPIFF. This technique utilizes inert gas-halogen excimer lasers, a relatively new but optically simple and very efficient source of coherent and intense beams of UV photons. This concept has been the focus of a considerable number of laboratory investigations during the past few years[3-7]. The work reported here demonstrates that the UV-MPIFF

phenomenon also occurs in organophosphorus compounds which have structural features in common with true chemical threat agents.

2. SUMMARY OF RESULTS

As shown in Figure 1, an ArF laser beam at 193 nm and at a repetition rate of 1 Hz was directed into a six-way vacuum cross containing the organophosphorus compound being studied. The cell was usually filled in a static mode, but for low concentration experiments the gases were flowing. Two compounds were studied, dimethylmethylphosphonate (DMMP) and diethylmethylphosphonothioate (DEMPS).

Fluorescence from the fragments produced by the dissociation was collected by a quartz lens and focussed into a 1m monochromator. The dispersed fluorescence was detected by a gated photomultiplier tube. Generally, five pulses were averaged. The scan speed was adjusted so that the averaging did not degrade spectral resolution. The data were digitized and stored on our minicomputer for plotting.

Excited fragments detected from DMMP were C, C_2 and CH, as shown in Figure 2. DEMPS multiple photon dissociation produced excited C_2, CH and PO β band emission and possibly CS, PS or PO γ band emissions, as shown in Figure 3. Preliminary results show that detectable emission remained even in the presence of 100 torr of air, as shown in Figure 4. Dynamic dilution experiments showed that the intensity of the PO β band emission from DEMPS is linear in concentration and is therefore calibratable. These data are plotted in Figure 5.

The main objectives of the research project were accomplished. We showed that the multiple photon fragment fluorescence process occurs in at least two organophosphorus compounds and is likely to be a generally occurring effect. Moreover, the spectrum of the excited fragments depends on the parent molecule, which allows the possibility of compound identification by this technique. The process was shown to be linear in parent molecule

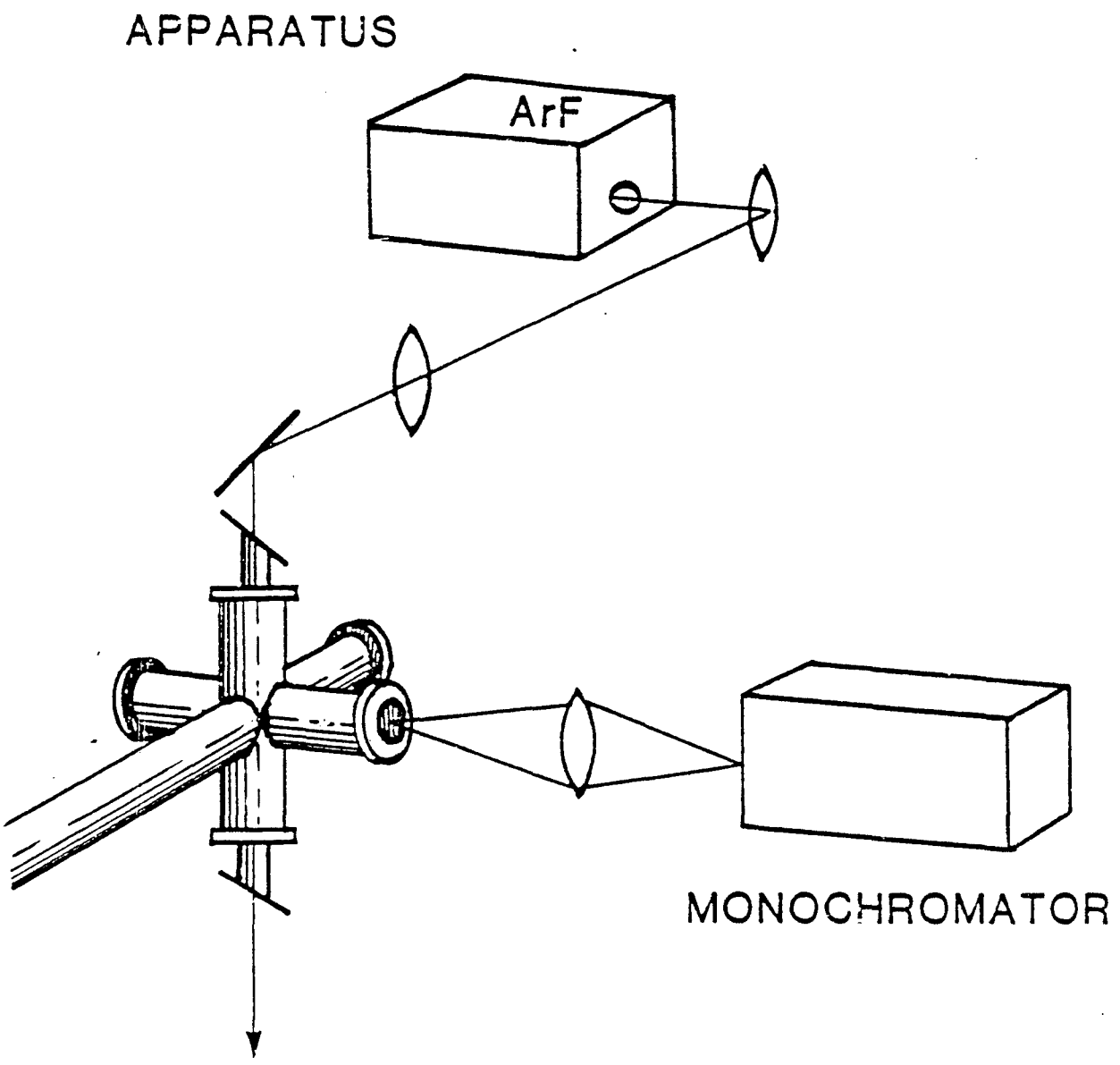


Figure 1. Experimental Apparatus.

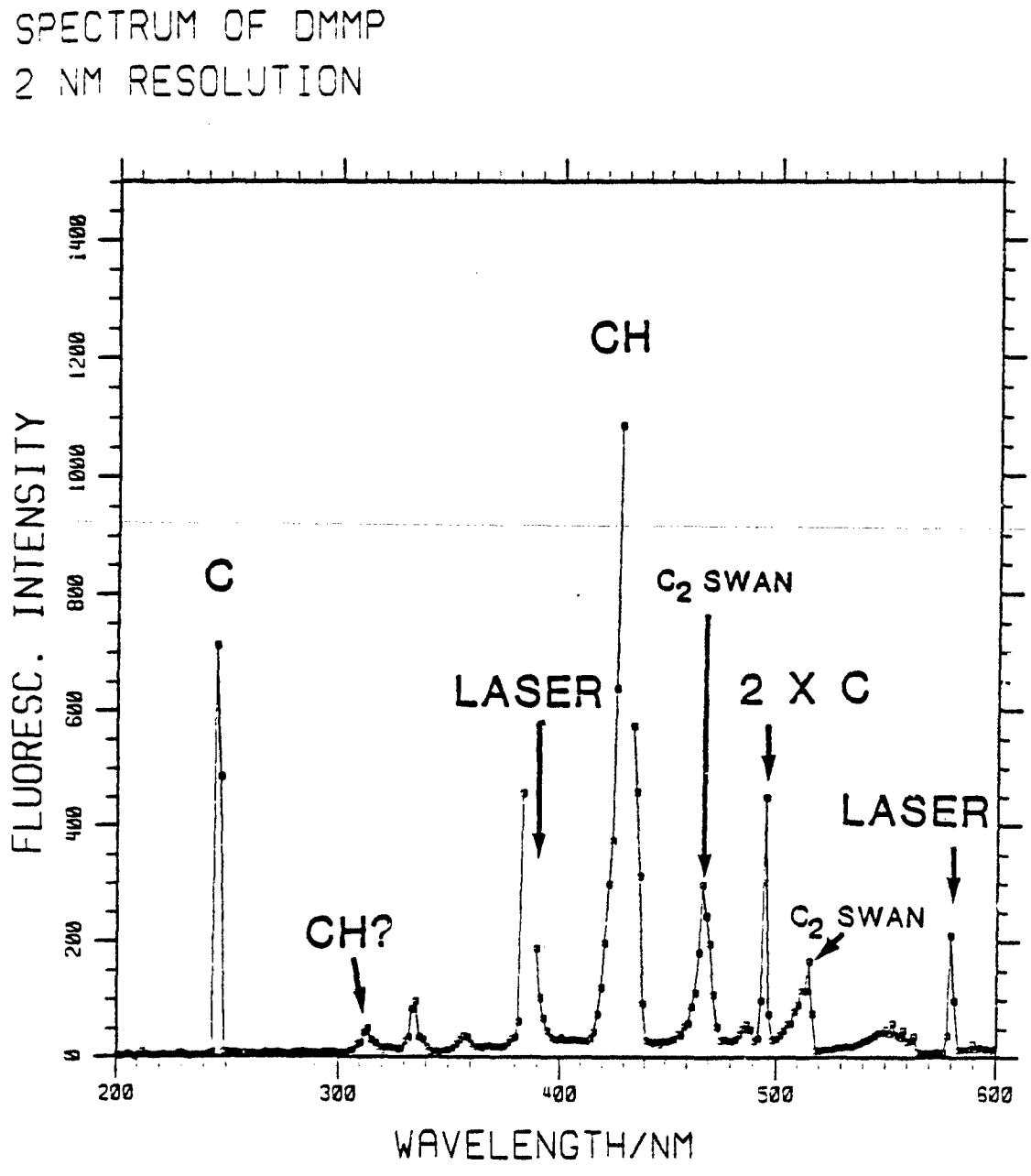


Figure 2. Low Resolution UV-MPIFF Spectrum of DMMP.

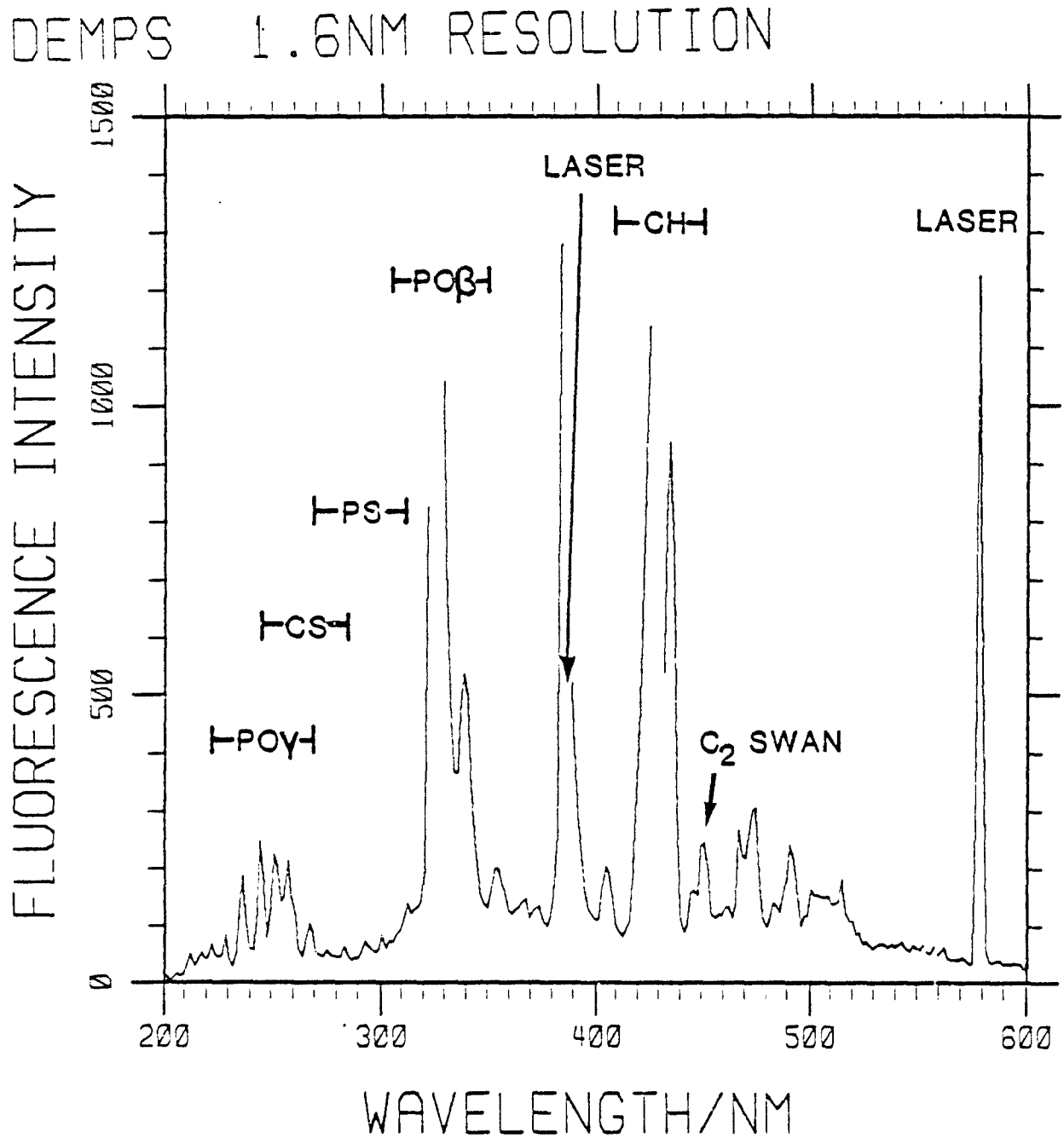


Figure 3. Low Resolution UV-MPIFF Spectrum of DEMPS.

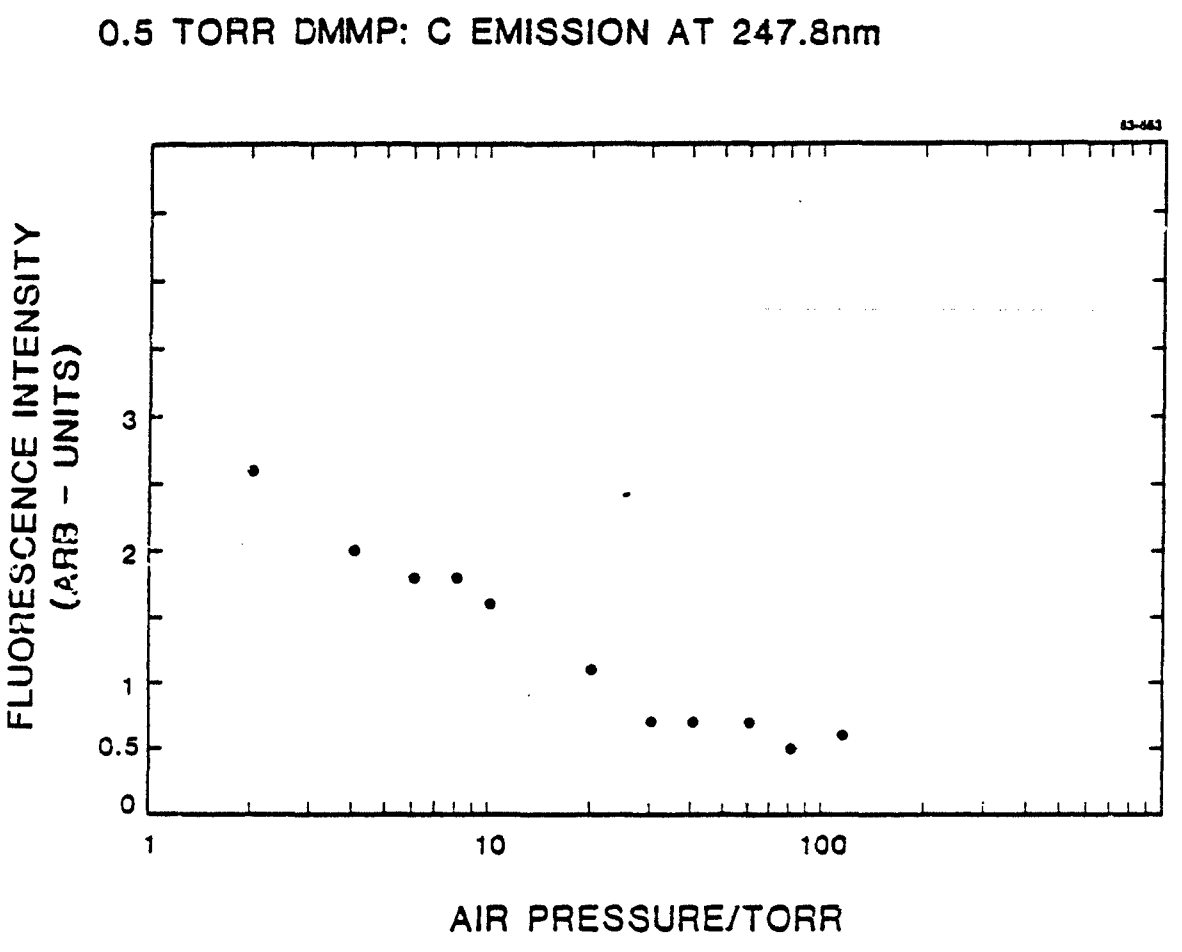


Figure 4. Quenching of Atomic C Fluorescence by Air.

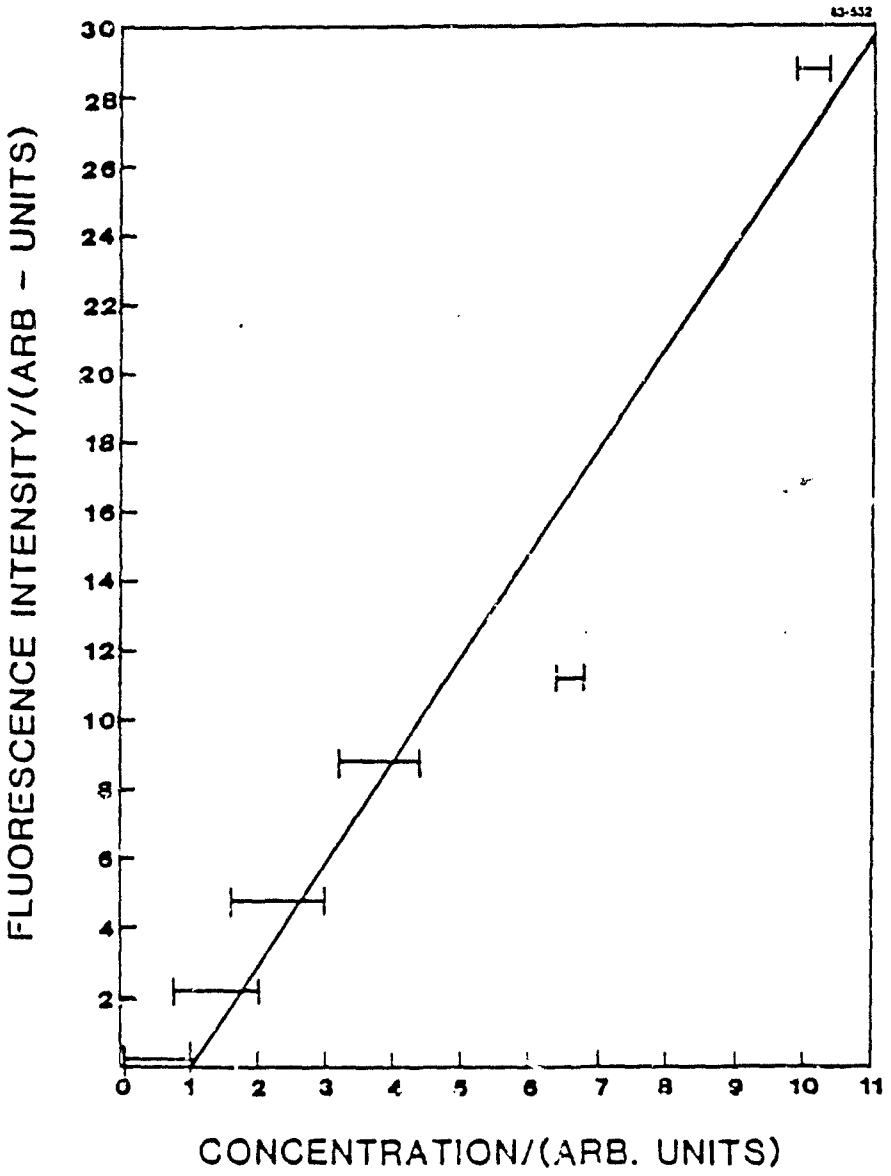


Figure 5. Variation of UV-MPIFF Intensity at 430 nm with the Concentration of DEMPS.

concentration, permitting calibration, and has measurable intensity in the presence of 100 torr of air. The UV MPIFF process has the potential to become a sensitive detection scheme for organophosphorus compounds.

3. RECOMMENDED FUTURE WORK

The experiments described in Section 2 demonstrate that the UV-MPIFF phenomenon is a viable candidate detection scheme for chemical threat agents. However, we must know whether it is capable of detecting sub-part per billion concentrations of threat agents before it can be judged truly useful. The basic considerations and experimental approach to this problem are outlined in the rest of this section.

3.1 Detection Sensitivity

The density of molecules which can be dissociated into excited fragments will be a complicated function of conditions under experimental control, such as laser wavelength and intensity, and molecular parameters such as absorption and quenching cross sections, and branching ratios into fluorescing states of the fragments. To get an idea of how these parameters might interact in the kinetic scheme, we present a treatment patterned after that of Jackson and co-workers.[8]

$$AF + h\nu \xrightarrow{\sigma_1} AF^* \qquad (1)$$

$$AF^* \xrightarrow{k_d} AF$$

$$AF^* + h\nu \xrightarrow{\sigma_2} AF^{**} \qquad (2)$$

$$AF^{**} \xrightarrow{k} A + F^{*}$$

$$F^{*} \xrightarrow{k_r} F + h\nu_F \tag{3}$$

$$F^{*} + M \xrightarrow{k_q} F + M \tag{4}$$

The number of excited fragments, N_{F*}, and the number of fluorescence photons per laser pulse, N_f, are given by

$$N_{F*} = \sigma_1 \sigma_2 \beta I^2 \tau_\ell \frac{N_{AF}}{k_d} \tag{5}$$

$$N_f = N_{F*} \frac{k_r}{k_r + k_q [M]} \tag{6}$$

where:

σ_1 = single UV absorption cross section for target molecule

σ_2 = UV absorption cross section for excited target molecule

β = quantum yield of excited fragment F*

I = laser intensity (photons/sec/cm^2)

T_ℓ = laser pulse time

k_d = predissociation rate for target molecule

N_{AF} = initial concentration of target molecules

N_{F*} = initial number of excited fragments

k_r = radiative decay rate for F* ($1/\tau_{rad}$)

k_q = quenching rate constant for F*

$[M]$ = concentration of quenching species

N_f = number of fluorescence photons per pulse

While the detailed cross sections, quantum yields and quenching rate constants for chemical threat species are largely unknown and are in fact the objective of this proposal, we can estimate a set to indicate the expected magnitude of the fluorescence signal.

Thus for:

$\sigma_1 = 10^{-17}$ cm^2

$\sigma_2 = 10^{-16}$ cm^2

$\beta = 10^{-2}$

$I = 1.5 \times 10^{25}$ photons/sec/cm^2 (Lumonics 260 with 1.0 cm^2 beam)

$T_\ell = 2 \times 10^{-8}$ sec

$k_d = 10^{+9}$ sec^{-1}

$N_{AF} = 2.5 \times 10^{11}$ (corresponding to 10 ppb mixing ratio in a 1 cm^3 volume)

We get for a single laser pulse, without multipass optics:

$$N_{F*} = 10^{-17} \times 10^{-16} \times 10^{-2} \times 2 \times 10^{50} \times$$

$$2 \times 10^{-8} \times 2.5 \times 10^{11} \times 10^{-9} = 1 \times 10^{10} \quad (7)$$

From our single photon fluorescence experiments for NO ($A\ ^2\Sigma^+$) in air at one atmosphere, we find about 1% of the excited fragments, N_{F*}, fluoresce, with the predominant quencher being O_2. Thus, for a "typical"

fluorescing fragment we can estimate a per pulse yield of fluorescence for each fragment, N_F, of order:

$$N_F = 0.01\ N_{F*} = 1 \times 10^8 \text{ photons} \qquad (8)$$

The fragment fluorescence photon yield per pulse estimated by Eq. (8) is, of course, very crude. Variations in absorption cross sections, fragmentation yields and quenching rates could certainly cause N_F to vary by many orders of magnitude. Experiments to determine these parameters for a number of nerve agent simulants are outlined in the next subsection.

3.2 Experimental Design

The experimental system for measuring quenching rates is basically the same as that used in the proof of principle experiments described earlier and shown in Figure 1. Improvements to the system will include a new sample cell designed for low to atmospheric pressure static fills rather than flow conditions. A fast response photomultiplier will also be needed to determine the quenching rates. The measurement procedure is straightforward. For a given partial pressure of simulant, the partial pressure of air will be increased and the resulting fluorescence intensity will be collected by a lens, dispersed by a monochromator and detected by a phototube. The data will be of the general form shown in Figure 4.

To measure absorption coefficients is easily done with beam splitters and detectors placed in the laser beam before entering and after emerging from the sample cell. The data acquisition system for measurements of this kind has already been assembled at Aerodyne for an infrared experiment.[9] Choosing detectors suitable for UV photons will immediately adapt the system to the absorption of excimer laser light. This sort of system will make simple the task of observing the expected nonlinear increase of the absorption coefficient as the laser intensity is varied. Variation in laser intensity can be controlled by the gas mixture, the voltage of the discharge, and filters, if necessary. The beam area can also be controlled and varied with telescopes.

In the case of focussed radiation, the laser intensity can also be varied by changing the focal length of the lens and by the use of field stops. When using lenses, major uncertainties will arise in estimating the minimum spot size (and hence the laser intensity) because of unavoidable and uncharacterized lens aberrations. It will probably be necessary to measure the spot size first using a pinhole on a micrometer-driven translation stage.

Having measured the absorption coefficient for a number of simulants, the quantum efficiency of the UV-MPIFF process can be estimated from the excitation/detection geometry and the phototube efficiency. As the data of Figures 2 and 3 show, this quantity will depend on the simulant and the excited fragment being considered.

The goal of these measurements is to provide the key parameters needed to estimate the lower limit of detection for the UV-MPIFF process. The formalism for making the estimate will be of the type described in Subsection 3.1 above.

The fluorescence output is imaged and detected at right angles to the input laser beam. A short wave cut-off filter and optical baffles may be included to discriminate against Rayleigh and Mie scattered laser light. Of course any operational detector would be multiplexed with either an OMA or a spectral correlator detection scheme to detect the entire fluorescence spectrum from each laser pulse.

3.3 Simulant Selection and Experimental Rationale

The major purpose of the proposed work is to demonstrate the level of unique UV/MPIFF signals from compounds representative of threat chemical species. For obvious reasons we have no desire to work with the threat agents themselves, at least not in such a preliminary study. Any experimentation with real chemical agents requires extensive security and safety precautions available only at specialized facilities.

However, personnel at the Army's Chemical Systems Laboratory have identified relatively innocuous simulant compounds which share general chemical and physical characteristics with known nerve and blister agents.

Among such compounds are dimethylmethyl phosphonate and diisopropylmethyl phosphonate, diethylmalonate and 2-chloroethylsulfide. The phosphonate compounds, representing organophosphorus nerve gases, are expected to yield fluorescence from the PO ($A\ ^2\Sigma^+$, $B\ ^2\Sigma^+$, $B'\ ^2\Pi$), CH ($A\ ^2\Delta$, $B\ ^2\Sigma^-$), C_2 ($d\ ^3\Pi_g$), and possibly HCO ($\tilde{A}\ ^2A'$) states. The 2-chloroethylsulfide is similar to mustard gas and should be characterized by emissions from CS ($A\ ^2\Pi$), CCl ($A\ ^2\Sigma^+$), CHCl ($\tilde{A}\ ^1A''$) and CH. Mixtures in the 1 ppb to 10 ppm range of these compounds with zero air, nitrogen, argon, and/or helium represent feasible and defensible standins for airborne threat agents. Mixtures of common airborne species which are potential interferants could also be prepared. Potential interferant species include NO, NO_2, CO, CO_2, SO_2, and simple hydrocarbons.

Investigation of the UV-MPIFF spectra of these mixtures as a function of laser wavelength and pulse power, background gas and gas pressure, and possibly interferant level would clearly allow a judicious appraisal of whether or not the UV-MPIFF detector concept deserves serious consideration for development.

4. PUBLICATIONS

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b. "Ultraviolet Multiple Photon Induced Fragment Fluorescence in Organophosphorus Compounds", D.S. Frankel and C.E. Kolb, submitted to the Journal of Physical Chemistry, January 1984.

5. PARTICIPATING SCIENTIFIC PERSONNEL

Scientists who participated in this work were:

Donald S. Frankel

Charles E. Kolb

Andrew Freedman

Mark Zahniser

No advanced degrees were earned during this project.

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